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FINAL REPORT ON THE
SPECIAL CONTRACT, SPC–92–4020,

ENTITLED

SIFT AND FALP STUDIES OF
PLASMA REACTION PROCESSES

by

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and

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The data acquisition and analysis techniques used with the Innsbruck SIFT and FALP apparatuses have been considerably refined, following which a detailed SIFT study has been carried out of the reactions of halogen ions with Cl_2 and Br_2, and preliminary measurements of electron temperatures, electron energy distribution functions and electron attachment coefficients have been performed using the FALP apparatus. Following these developments and studies, the new data acquisition and analysis techniques have been successfully installed onto the FALP apparatus at the Phillips Laboratory Geophysics Directorate.

FORM 1473

CONTENTS

I. Introduction

Under the terms of this Special Contract, SPC–92–4020, we were required to perform, in Innsbruck, investigations of some specific ion–molecule reactions (using our SIFT apparatus), some electron attachment reactions (using our FALP) apparatus, to refine the data acquisition and analysis method for the SIFT and FALP apparatuses, to install and verify operation of these techniques onto the SIFT and FALP apparatuses at the Phillips Laboratory Geophysics Directorate, and to provide five copies of a Final Report on the results of this work.

II. Results of the Innsbruck Studies.

(i) Selected Ion Flow Tube (SIFT) Studies.

We have carried out a detailed study at of the reactions of the halogen positive ions, F^+, Cl^+, Br^+, I^+, Cl_2^+ and Br_2^+, and the halogen negative ions, F^-, Cl^-, Br^-, I^-, Cl_2^- and Br_2^-, with Cl_2 and Br_2 at 300 K. The detailed results of this study and some conclusions drawn from it are presented in a research paper, included as Appendix A to this report , which has been accepted for publication to the Journal of Chemical Physics.

(ii) Flowing Afterglow/Langmuir Probe (FALP) Studies.

A new technique has been developed to determine the electron energy distribution functions ,f(E), in flowing afterglow plasmas. This involves the determination of the second derivative ,d^2I/dV^2, of the current (I) against voltage (V) of a Langmuir probe immersed in the plasma. When a plot of d^2I/dV^2 is linear, the f(E) is Maxwellian, and from the slope of the plot the electron temperature, T_e, is obtained. Sample data obtained in helium and argon afterglow plasmas are shown in Fig. 1 where it can be seen that in argon afterglows high T_e can be obtained. This has provided us with the opportunity to study electron attachment reactions both as a function of the attaching gas temperature, T_g, and T_e in the FALP apparatus. Preliminary results of such studies are startling. Fig. 2 shows the
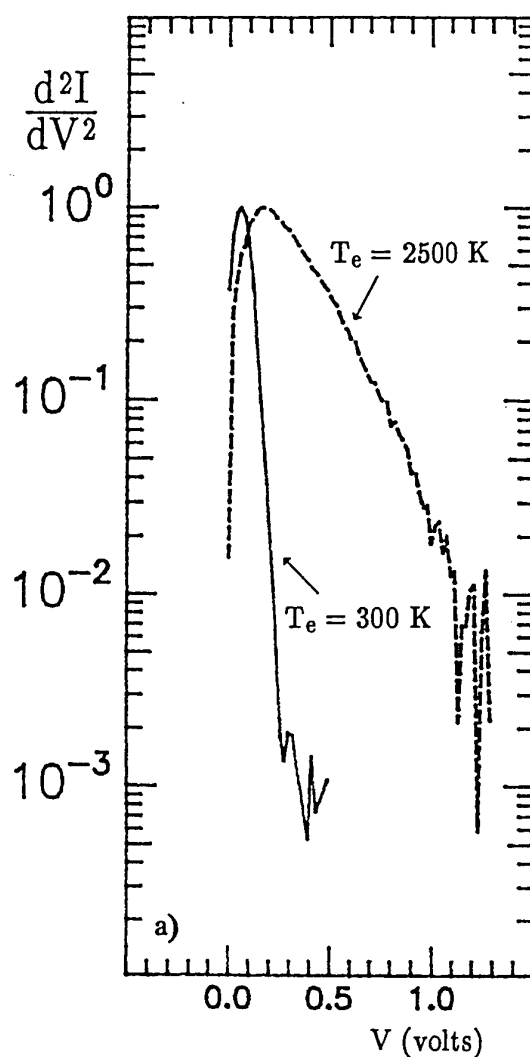
Figure 1. Plots of the second derivative of the probe current, I, with respect to the probe voltage, d^2I/dV^2, against probe voltage, V, obtained in the FALP plasmas. The plots have been normalised do $d^2I/dV^2=1$ at the peaks of the curves. Note the rapid reduction of d^2I/dV^2 (to the left of each figure) as the probe voltage is swept through space potential (zero on the V scale). Data were obtained in pure helium (steep line) and pure argon afterglow plasmas at a $T_g=300$ K in both cases. The linearity of the plots indicates that f(E) is closely Maxwellian, at a $T_e=300$K in the helium afterglow and $T_e=2500$K in the argon afterglow.
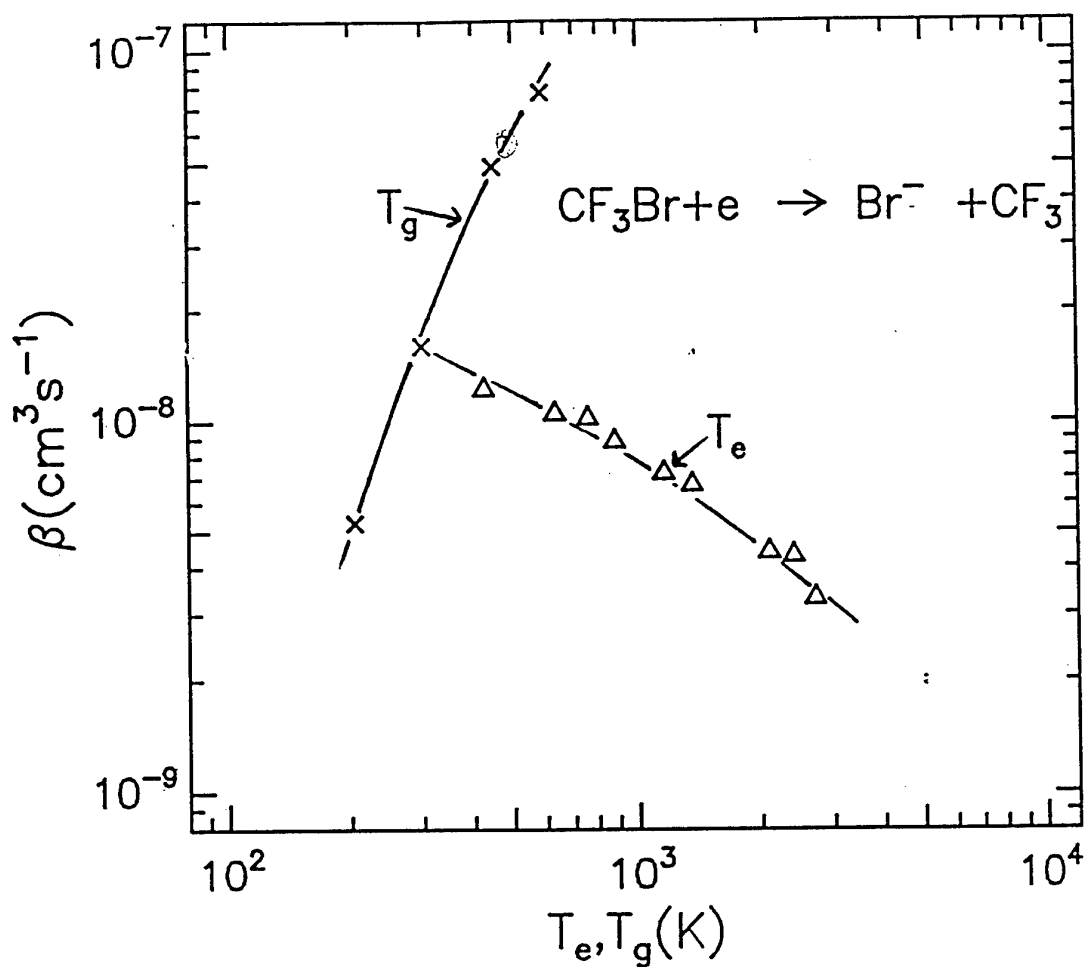
Figure 2. The variation of the attachment coefficient, β, for CF_3Br with both the gas temperature, T_g (x, obtained in helium carrier gas at a pressure about 1 torr), and the electron temperature, T_e (Δ, obtained in Argon carrier gas at a pressure of about 0.3 torr and a T_g of 300 K). Both sets of data were obtained using the FALP apparatus. The only ionic product observed in both experiments was Br^- (dissociative attachment). The rapid increase of β with T_g implies an activation energy of 80 meV for the reaction. The decrease of β with T_e implies a reduction in the rate of capture of the electrons by the molecule.

data obtained for dissociative electron attachment to CF_3Br, where it can be seen that the attachment coefficient, β, <u>increases</u> rapidly with T_g and <u>decreases</u> with T_e. This data alone forcibly indicates that if the rates of electron attachment to particular molecules are to be obtained in hot plasmas (such as rocket plumes) then not only it is necessary to know both T_g and T_e in such plasmas but also to know how β varies with both T_g and T_e.

III. Work at the Phillips Laboratory.

We visited the laboratory of Dr. John F. Paulson at the Phillips Laboratory Geophysics Directorate at Hanscom Field, Mass. in October 1992 to install our newly–developed data acquisition and analysis techniques onto that laboratories FALP apparatus. This involved the construction and installation of some hardware (preamplifier, interface board) and the installation of a <u>major</u> software package which was developed in Innsbruck by Dr. Španěl over a six–month period. This was an extremely successful enterprise. Data acquisition and analysis of FALP data at the Phillips Laboratory has been speeded up very considerably with the obvious benefit to the research programme, and to the complete satisfaction of the scientific staff of the laboratory.

During the visit we also advised on how the data acquisition and analysis techniques for the other flow tube experiments in the laboratory (i.e. the SIFT and HTFA experiments) should be upgraded and delivered two seminars on the results of our work carried out under the terms of Special Contract.

IV. Concluding Remarks.

Essentially all the requirements outlined in the original contract proposal have been accomplished. The data acquisition and analysis techniques for both the SIFT and FALP experiments have been considerably upgraded, following which the proposed scientific programmes on the Innsbruck SIFT and FALP apparatuses have been carried out and our new expertise on the data acquisition and analysis has been very successfully introduced into the Phillips Laboratory Geophysics Directorate.

APPENDIX A:

Journal of Chemical Physics, in print.

The Reactions of Positive and Negative Halogen Ions with Cl_2 and Br_2

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ABSTRACT

A selected ion flow tube (SIFT) study has been carried out at 300 K of the reactions of some atomic and molecular positive and negative halogen ions with Cl_2 and Br_2 from which the rate coefficients, k, and ion product distributions have been determined.

For the energetic F^+ ion reactions, dissociative charge transfer is the dominant process, while for the Cl^+ ions, only non–dissociative charge transfer occurs. For the less energetic Br^+ and I^+ reactions, dihalogen molecular ions are important products. All these positive ion reactions proceed quite efficiently, i.e. the k are appreciable fractions of k_c, their respective collisional rate coefficients, except for the reactions of Cl_2 with the lower energy ions of the spin–orbit triplet of I^+, i.e. $I^+(^3P_{1,0})$, for which $k \sim 0.07 k_c$, this being due to the endothermicities of the reactions. The molecular ion Cl_2^+ undergoes rapid non–dissociative charge–transfer with Br_2, a process which is, of course, endothermic for the reaction of Br_2^+ with Cl_2 and so no reaction is observed.

The less energetic atomic negative ion reactions proceed –via atom exchange– in which the atomic negative ion of the reactant molecular species and a dihalogen molecule are produced. For those reactions that are exothermic, the k are, within error, equal to $2/3$ k_c, implying that they proceed via complexes which separate statistically back to reactants $(1/3)$ and forward to products $(2/3)$. Both the Br^-+Cl_2 and Cl^-+Br_2 reactions are somewhat less efficient, (i.e. $k < 2/3 k_c$), a resulting of the slight endothermicities of the reactions. Of the molecular negative ion reactions, electron transfer is the major process in the Cl_2^- reaction with Br_2, whereas the reaction of Br_2^- with Cl_2 proceeds relatively slowly producing the triatomic ion $BrCl_2^-$.

I. INTRODUCTION

There have been several studies of the reactions of the atomic positive ions of the halogens with a variety of gases at thermal energies [1,2,3]. The reactions of F^+ have received most attention [4,5]. The most recent study has been a selected ion flow tube (SIFT) survey of the reactions of F^+, Cl^+, Br^+, and I^+ with some fifteen molecular gases at 300 K in which a variety of reaction processes were observed [6]. Curiously, however, there have been no surveys of the reactions of atomic halogen ions with halogen molecules, even though such reactions must be occurring in ionized gases containing halogens such as some laser plasmas and surface etchant plasmas. Also, to our knowledge, the reactions of the halogen molecular positive ions have not been investigated with any gases. The reactions of the atomic and molecular halogen negative ions (with the halogens) also have received little attention, although the reactions of F^- and Cl^- with Cl_2 [7], the isotope exchange reactions of $^{37}Cl^-$ with a variety of chlorine–containing molecules, including Cl_2 [8] and, very recently, the reactions of F^-, Br^- and I^- with Cl_2 [9] have been studied. The results of these studies will be mentioned in Section III. B.

In this paper we report the results of a study of the reactions at 300 K of the halogen positive ions F^+, Cl^+, Br^+, I^+, Cl_2^+ and Br_2^+, and the halogen negative ions F^-, Cl^-, Br^-, I^-, Cl_2^- and Br_2^- with Cl_2 and Br_2. This comprehensive study was carried out using our SIFT apparatus at the University of Innsbruck.

II. EXPERIMENTAL

The SIFT apparatus used for these studies is of conventional design as is described in detail in a recent review [10]. Reactant ions are generated in an electron–impact ion source, and ions of a particular mass–to–charge ratio are selected by a quadrupole mass filter and injected through a venturi–type inlet into fast–flowing helium carrier gas at a pressure of ≈ 0.5 Torr. Thus, a swarm of thermalised ions is convected along the flow tube

and the ions are sampled downstream by a pinhole orifice/differentially pumped mass spectrometer/detection system. Reactant gases are introduced into the carrier gas at a controlled, measured rate whence the thermalised primary ions are lost in reaction with the reactant gas. The loss rate of the primary ions and the ion products of the reactions are monitored by the downstream detection system and the rate coefficients and the ion product distributions are determined in the usual way [10].

The F^+, F^-, Cl^+ and Cl^- reactant ions were derived from CCl_2F_2, the Br^+ and Br^- from C_2H_5Br, and the I^+ and I^- from CH_3I in order to minimise corrosion of the ion source. However, the molecular ions Cl_2^+, Cl_2^-, Br_2^+ and Br_2^- had to be derived from Cl_2 and Br_2. The Cl_2 gas was obtained from a commercial cylinder of liquid Cl_2 (Linde company, 99.8% pure), and the Br_2 gas was obtained from above liquid bromine. No effort was made to purify these gases; in all the reactions studied no significant fractions ($\geq$ 2%) of unidentified "foreign" ions were detected from which we conclude that these gases were $\geq$ 98% pure halogens.

As mentioned previously, all the reactions were studied at room temperature (300±2 K). The estimated uncertainty in the measured k accounting for all possible systematic errors is ±15%, although relative values of the measured k are more accurate (±5%).

III. RESULTS AND DISCUSSION

The ground states of the singly–charged atomic halogen positive ions have $^3P_{2,1,0}$ configurations. The precise ionization energies of the halogen atoms are given in Table I. The F^+ and Cl^+ spin–orbit states are very closely spaced in energy, whereas those for Br^+ and especially I^+ are much more widely spaced. So differences in the reactivity of the Br^+ and I^+ ions in the different spin–orbit states are sometimes discernible [2]. Of course, such depends on whether or not ions in all three spin–orbit states are injected into the SIFT, which in turn depends on the conditions under which the ions are created in the ion source.
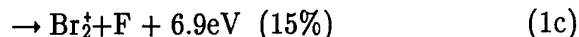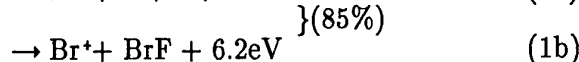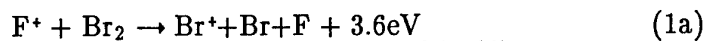
At high source gas pressures , collisions of the $^3P_{0,1}$ excited ions with source gas molecules can result in their quenching to the lowest $^3P_2$ state. Such an effect was observed in the present experiments for I^+ ions, as is indicated by the results for the $I^+ + Cl_2$ reaction (see below and Table II). Similar comments relate to the Cl_2^+ and Br_2^+ ions. Both these ions have $^2\Pi_{3/2,1/2}$ configurations; the Cl_2^+ is a closely–spaced doublet but the splitting in the Br_2^+ is appreciable, i.e. $Br_2^+(^2\Pi_{3/2})$ has a recombination energy of 10.54 eV and that for $Br_2^+(^2\Pi_{1/2})$ is 10.95 eV [11]. Again, the higher–energy molecular ion would probably be efficiently quenched in collisions with parent gas molecules (presumably by near–resonant charge transfer). Of course, the singly–charged atomic halogen negative ions are singlets and no complications arise. Long–lived excited states of Cl_2^- and Br_2^- are not expected and no complications are expected in their reactions also.

A further point to make is that a fraction of both the Cl_2 and Br_2 molecules are vibrationally excited at 300 K. Thus $\approx$ 7% of the Cl_2 molecules and $\approx 21\%$ of the Br_2 molecules are in their v=1 vibrational states at 300 K, with energies 70 meV and 40 meV above their ground vibrational states respectively [12]. Although small, the energies of these vibrationally excited molecules can render some near–thermoneutral reactions just exothermic; some such examples exist in the present data.

### A. The reactions of F^+, Cl^+, Br^+, I^+, Cl_2^+ and Br_2^+ with Cl_2 and Br_2.

The measured rate coefficients, k, and the ion products of these reactions are given in Table II together with the respective Langevin collisional rate coefficient, k_c, appropriate to non–polar molecules [13]. The ratio k/k_c is an indicator of the efficiency of the reaction. For only one of the reactions (i.e. $Cl^+ + Br_2$) is $k/k_c = 1$ and for the other seven reactions k/k_c exceeds 0.3.

In the reactions of F^+ with Cl_2 and Br_2, both atomic and molecular ions are produced. The reactions presumably proceed via charge transfer producing electronically excited Cl_2^+ and Br_2^+ ions which are largely predissociated producing the atomic ions, e.g.:

$$F^+ + Br_2 \rightarrow Br^+ + Br + F + 3.6eV \qquad (1a)$$
$$\left.\rule{0pt}{20pt}\right\}(85\%)$$
$$\rightarrow Br^+ + BrF + 6.2eV \qquad (1b)$$

$$\rightarrow Br_2^+ + F + 6.9eV \quad (15\%) \qquad (1c)$$

However, it is possible that the dihalogen molecule is produced, as is indicated as reaction (1b) in this example. For both reactions, k/k_c is significantly less than unity (see Table II), perhaps implying unfavourable Franck—Condon factors for the charge transfer reactions.

The less energetic Cl^+ reactions both apparently proceed via non—dissociative charge transfer (dissociative charge transfer is endothermic). The Br_2 reaction proceeds with unit efficiency (i.e. $k = k_c$):

$$Cl^+ + Br_2 \rightarrow Br_2^+ + Cl + 2.4eV \qquad (2a)$$
$$-\!\!/\!\!\rightarrow Br^+ + BrCl + 1.4eV \qquad (2b)$$
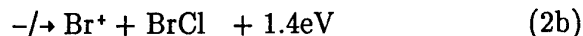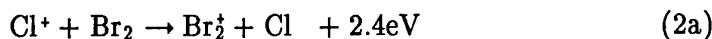
In this reaction the $^2\Pi_u$ electronic states of Br_2^+ are energetically accessible and so the charge transfer can proceed to produce the $Br_2^+(^2\Pi_u)$ ions. (The appearance energies are; $Br_2^+(^2\Pi_{3/2;u}) = 12.41eV$, $Br_2^+(^2\Pi_{1/2;u}) = 12.8eV$ [11]; at these energies there is a strong peak in the photoelectron spectrum of Br_2[14]). Although the production of Br^+ and the dihalogen molecule $BrCl$ is quite exothermic it does not occur, as is indicated by equation (2b). The corresponding $Cl_2^+(^2\Pi_u)$ states are at energies greater than the recombination energies of ground state Cl^+ ions and therefore inaccessible in the $Cl^+ + Cl_2$ reaction. Thus the charge transfer must proceed with the production of $Cl_2^+(^2\Pi_g)$ ground state ions, presumably in vibrational states for which the Franck—Condon overlap with the Cl_2 ground state is not high; hence a possible reason why k/k_c is less than unity (see Table II)

The Br^+ reaction with Cl_2 is interesting in that both Cl_2^+ and the dihalogen ion $BrCl^+$ are produced:

$$Br^+ + Cl_2 \rightarrow Cl_2^+ + Br + 0.36eV \ (55\%) \qquad (3a)$$
$$\rightarrow BrCl^+ + Cl + 0.44eV \ (45\%) \qquad (3b)$$
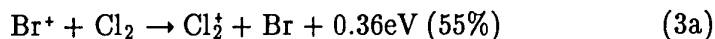
The two observed product channels are not greatly exothermic for ground state reactants and products; the third conceivable arrangement of the products to produce $Cl^+ + BrCl$ is clearly endothermic. Thus the reaction probably proceeds via a loose $(BrCl_2)^+$ complex which separates with approximately equal probability to the products. The Br^+ reaction with Br_2 apparently proceeds via charge transfer to produce Br_2^+, but mixing of the Br atoms in a loose Br_3^+ complex could occur prior to separation to the products. (Note: In our recent study of the reactions of the singly-charged rare gas ions with the halogens, Br_2^+ was seen to be a stable ion which is unreactive with Br_2 [15]. Note, also, that isotopic labeling of the Br^+ reactant ions could indicate whether or not mixing of the Br atoms in a Br_3^+ complex occurred, but this was not possible with the present SIFT injector resolution. Such studies were possible for the Cl^- reaction with Cl_2 described below).
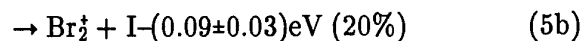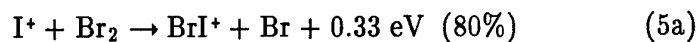
No evidence was obtained for the presence in the flow tube of more than one spin-orbit state of the reactant F^+, Cl^+ and Br^+ ions in these experiments. Such is usually indicated by curvature in the semi-logarithmic decay plots of reactant ion current versus reactant gas flow rate from which the rate coefficient for the reactions are obtained [2,10]. Obviously, for such curvature to be observed, the different spin-orbit states of the ions must react at different rates with the reactant gases. Often, though, the reactions of the ions in each of the spin-orbit states all occur at the collisional rate [6] and then, of course, no curvature of the decay plots occurs. However, for the reaction of I^+ with Cl_2 clear curvature of the decay plots was evident; the curvature could be exaggerated by operating the ion source at low pressure of the source gas (CH_3I). Analysis of the curved decay plots indicated that effectively two separately reacting species of I^+ were present in the flow tube. The

most abundant species present, presumably the ground state ion $I^+(^3P_2)$ (which has the highest statistical weight and which could be made very dominant in the flow tube by increasing the pressure in the ion source, presumably because of its enhancement due to collisional quenching of the $I^+(^3P_{1,0})$ ions), reacted only slowly with the Cl_2 (i.e. $k=0.06k_c$). The higher energy ions $I^+(^3P_{1,0})$ reacted much faster, $k\sim(0.25-0.50)k_c$ (see Table II). The uncertainty in the latter rate coefficient is due to the relatively small fraction of these ions in the flow tube and the associated difficulty in determining k accurately. Only ICl^+ was observed as the product of these reactions; e.g.:

$$I^+(^3P_2)+Cl_2 \rightarrow ICl^+ + Cl + 0.01eV \qquad (4)$$
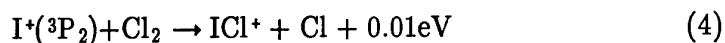
Reaction (4) for the lowest energy I^+ ions apparently is almost exactly thermoneutral using the data given in Table 1, yet the measured k is only about 6% of k_c. Significantly, about 7% of the Cl_2 molecules are in the $v=1$ vibrational state with an energy of 0.07eV above the ground state, and it is therefore probable that the reaction that is being observed is not only reaction (4) but also in part the corresponding exothermic reaction involving $Cl_2(v=1)$. It is also possible that reaction (4) is slightly endothermic implying that either the ionization energy of ICl is slightly greater than the 10.07 given in Table 1 or the bond energy of ICl is slightly less than the published value. The reactions of higher energy ions $I^+(^3P_{1,0})$ with Cl_2 to produce ICl^+ are clearly exothermic, which is consistent with the much greater reaction rates for these ions compared to the $I^+(^3P_2)$ ions.

The I^+ reaction with Br_2 proceeds thus:

$$I^+ + Br_2 \rightarrow BrI^+ + Br + 0.33 \text{ eV} \quad (80\%) \qquad (5a)$$
$$\rightarrow Br_2^+ + I-(0.09\pm0.03)eV \quad (20\%) \qquad (5b)$$

The overall reaction rate is close to the collisional rate ($k\sim0.9k_c$; see Table II). The charge transfer channel (5b) is slightly endothermic for ground–state reactants, yet

it represents some 20% of the product distribution. This indicates that it is the higher energy $I^+(^3P_{1,0})$ ions which are responsible for the Br_2^+ product ions, but it is also perhaps significant that, as mentioned above, some 20% of the Br_2 are in their first vibrational state at 300K. Since the energy of this vibrational state is 0.04 eV above the ground vibrational state, then a fraction of the Br_2^+ product ions could result from the slightly endothermic reaction:
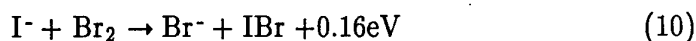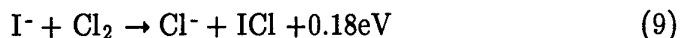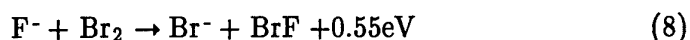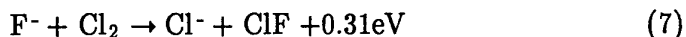
$$I^+(^3P_2) + Br_2(v=1) \rightarrow Br_2^+ + I - (0.05\pm0.03)eV \qquad (6)$$
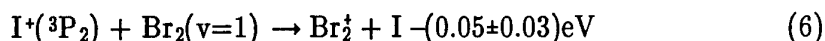
The reactions of the molecular positive ions Cl_2^+ and Br_2^+ are unspectacular (the reactions of the molecular negative ions are more interesting; see the next section). Cl_2^+ reacts with Br_2 by rapid charge transfer producing Br_2^+ (98%) and a trace of $BrCl^+(\sim2\%)$. Within the uncertainties of the energetics (the greatest uncertainty is the ionization energy of BrCl; see Table I), production of $BrCl^+$ and BrCl in this reaction is indeed exothermic by $(0.34\pm0.2)eV$. No reaction is observed between Br_2^+ and Cl_2 since charge transfer and the production of $BrCl^+$ are both endothermic (the latter by about 0.6 eV), as presumably is the production of the triatomic ions $BrCl_2^+$ and $Br_2Cl_2^+$. Similarly, formation of Cl_3^+ and Br_3^+ in the $Cl_2^++Cl_2$ and $Br_2^++Br_2$ interactions was not observed although these triatomic ions are known to be stable [15].

B. The reactions of F^-, Cl^-, Br^-, I^-, Cl_2^- and Br_2^- with Cl_2 and Br_2

All these negative ion reactions are characterized by small ergicities. Only half of the ten reactions are exothermic, whilst the other half are slightly endothermic or thermoneutral (within the differences in vibrational zero-point-energies). Thus energetic and statistical factors probably have the dominant influence on the rate coefficients and product ions for these reactions and not factors such as available electronic states states and Franck-Condon factors.

The measured rate coefficients (k) and product ion distributions, The Langevin collisional rate coefficients (k_c) and the ratios k/k_c are given in Table III. At the onset, it is to be noted that the measured k for the F^-, Br^- and I^- reactions with Cl_2 are essentially identical to those measured recently by Fussen et. al [9].

It is appropriate to discuss first the four exothermic reactions of F^- and I^- with Cl_2 and Br_2 since they have a second common feature. The atomic ion/molecule reactions proceed thus

$$F^- + Cl_2 \rightarrow Cl^- + ClF + 0.31eV \qquad (7)$$
$$F^- + Br_2 \rightarrow Br^- + BrF + 0.55eV \qquad (8)$$
$$I^- + Cl_2 \rightarrow Cl^- + ICl + 0.18eV \qquad (9)$$
$$I^- + Br_2 \rightarrow Br^- + IBr + 0.16eV \qquad (10)$$

All can be described as atom exchange reactions in which a different atomic negative ion and a dihalogen molecule is formed. However, the remarkable common feature of all four reactions is that they all proceed with nearly the same efficiency, that is the $k \simeq 2/3\ k_c$ (see Table III). This is as would be expected if the reactions proceed via the triatomic halogen complexes which separate statistically partly back to the reactants (1/3 of the complexes) and forward to the products (2/3 of the complexes) independent of the different exothermicities of the reactions. Making this drastic assumption we have calculated the k/k_c by considering the total partition functions of the reactants and products (see Appendix I). The values obtained are also given in Table III, and are seen to be in remarkably good agreement with the experimentally–derived values indicating that only statistical factors or the number of available states of the reactants and products control the course of the reaction.
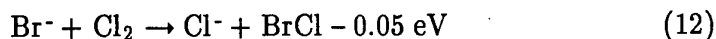
The reaction:

$$Cl^- + Br_2 \rightarrow Br^- + BrCl - (0.007 \pm 0.004)eV \qquad (11)$$
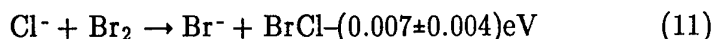
is apparently slightly endothermic for the ground vibrational state of Br_2 and this

must inhibit the reaction somewhat. Assuming the reaction efficiency is reduced only because of the endothermicity ($\Delta E = 0.007$ eV) and assuming that the measured k would equal $2/3k_c$ if it were thermoneutral, then the measured $k = 2/3k_c \exp{-\Delta E/kT}$. Thus at 300K, $k/k_c = 0.5$ which is consistent with the experimental value of 0.46 considering the uncertainty in the ΔE (see equation (11). Note, however, as previously stated, that some 21% of the Br_2 molecules are in the $v=1$ state (energy 0.04eV) at 300K and so for this percentage of the molecules reaction (11) is exothermic, presumably proceeding with a $k \sim 2/3k_c$. Reaction (11) would surely become more efficient at elevated temperatures when presumably k would approach $2/3k_c$. (or better the 'calculated' value of 0.669 given in Table III)

The reaction:

$$Br^- + Cl_2 \rightarrow Cl^- + BrCl - 0.05 \text{ eV} \qquad (12)$$

is more endothermic than reaction (11), and significantly, the reaction is less efficient ($k = 0.3k_c$), but again, the presence of vibrationally excited Cl_2 ($\sim 7\%$) should be accounted for. Reaction (12) for $Cl_2(v=1)$ is just exothermic (by 0.02 eV) and when this is accounted for together with the endothermicity of the reaction involving $Cl_2(v=0)$ then, again, the reduction in k below $2/3k_c$ (see Table III) can be explained.
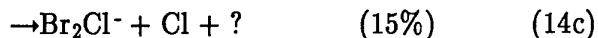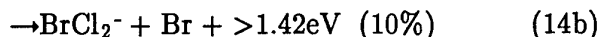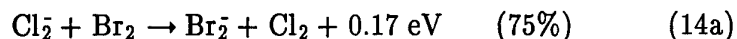
The reaction of $^{35}Cl^-$ with the naturally occurring isotopically–mixed Cl_2 ($^{35}Cl:^{37}Cl :: 3:1$) used in these studies, viz:

$$^{35}Cl^- + Cl_2 \rightarrow {}^{37}Cl^- + Cl_2 \qquad (13)$$

has a rate coefficient (see Table III) which is quite consistent with statistical isotope exchange within a complex in which the Cl atoms are equivalent (i.e. $k \simeq 0.167 \ k_c$, noting again that $^{35}Cl:^{37}Cl :: 3:1$). This is not consistent with the deductions made by Van Doren et al. [8] whose results for the study of the $^{37}Cl^- + Cl_2$ reaction were corresponding to the separation of Cl^- from a linear Cl_3^- intermediate in which total

scrambling apparently did not occur. However, the results for all the atomic negative ion/halogen molecule reactions included in this study indicate that total scrambling does occur with the intermediate complexes (hence the experimental results that $k \sim 2/3\ k_c$). Electron transfer between Cl^- and Cl_2 is quite endothermic as it is between Br^- and Br_2. The use of isotopic labeling would surely show that isotopic scrambling also occurs within the Br_3^- complex, but this could not be investigated in this study due to inadequate separation of $^{79}Br^-$ and $^{81}Br^-$ by the SIFT injector.

The reactions of the molecular negative ions proceed thus:

$$Cl_2^- + Br_2 \rightarrow Br_2^- + Cl_2 + 0.17\ eV \quad (75\%) \quad (14a)$$
$$\rightarrow BrCl_2^- + Br + >1.42eV \quad (10\%) \quad (14b)$$
$$\rightarrow Br_2Cl^- + Cl + ? \quad (15\%) \quad (14c)$$

The major process is exothermic electron transfer, the rate coefficient for this channel (14a) being some 75% of the total measured rate coefficient and is therefore $\sim 4 \times 10^{-10} cm^3 s^{-1}$, i.e. about $1/2 k_c$. A significant fraction (25%) (i.e. equivalent $k/k_c = 0.15$) of the Cl_2^-/Br_2 interactions result in the mixed trihalogen ions $BrCl_2^-$ and Br_2Cl^-. Using the available limit on the heat of formation of $BrCl_2^-$ (which is $<-4.8eV$ [16]) reaction (14b) is clearly exothermic and so surely is reaction (14c), although the heat of formation of Br_2Cl^- is not available. That these exothermic reactions are only minor channels is perhaps because rearrangement of the atoms in the tetraatomic complex is necessary which does not compete favorably with the simpler electron transfer process. The reaction

$$Br_2^- + Cl_2 \rightarrow BrCl_2^- + Br + >1.25eV \quad (15)$$
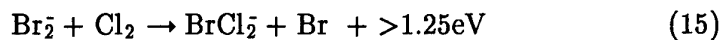
is clearly exothermic and yet it is inefficient ($k/k_c = 0.17$), again presumably due to the rearrangement required (or a small potential barrier exist which inhibits the reaction). Note that in this case electron transfer is endothermic (by 0.17 eV).

It is interesting to note that the ions Cl_3^- and Br_3^- were not observed in these studies, even though Cl_3^- is a known stable ion [8, 9, 17]; presumably Br_3^- is also stable. The reaction:

$$Cl_2^- + Cl_2 -/\rightarrow Cl_3^- + Cl - 0.54eV \qquad (16)$$

is apparently endothermic (as calculated using the literature value for the heat of formation of Cl_3^- of 3.12 eV [17]) and so presumably the corresponding reaction between Br_2^- and Br_2 is also endothermic. Certainly, these reactions did not proceed at a measured rate in these experiments at 300 K. Also the "mixed" ions $BrCl_2^-$ and Br_2Cl^- did not react at measurable rate with either Cl_2 or Br_2. It thus appears that these halogen triatomic ions are stable and unreactive with the halogen molecules. Of course, some such reactions will be endothermic as is the reaction:

$$BrCl_2^- + Cl_2 \rightarrow Cl_3^- + BrCl - >1.7 \text{ eV} \qquad (17)$$
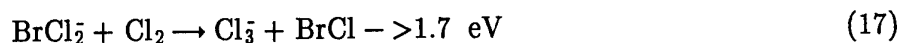
It would certainly be interesting to study several of these reactions at higher temperatures and at higher centre–of–mass energies in a SIFDT apparatus [10] to investigate whether or not k converges to $2/3k_c$ for the endothermic atom exchange reaction (11) and (12) and , for example, reaction (16) to see if Cl_3^- is formed.

IV. CONCLUDING REMARKS

The positive ion–molecule reactions included in this study proceed largely via charge transfer when that process is exothermic as it is for the F^+, Cl^+ and Br^+ reactions with the both Cl_2 and Br_2 and for the Cl_2^+ reaction with Br_2. However, for the I^++Cl_2 and I^++Br_2 reactions the charge transfer is endothermic (except for the $I^+(^3P_{1,0})+Br_2$ reactions) and the dihalogen ions ICl^+ and IBr^+ are the products.

The less energetic atomic negative ion reactions proceed largely via atom exchange in which the identity of the atomic negative ion changes and dihalogen molecules are formed. The most interesting result is that these reactions seem to

proceed via the formation of the triatomic halogen complexes (e.g. IBr_2^-) which separate with simple statistical probability back to reactants and forward to products, a process apparently not significantly influenced by the small exothermicities of these reactions.

These studies could usefully be extended to include the reactions of the atomic halogen ions with F_2 and those stable dihalogens with adequate vapour pressures e.g. ICl and IBr, to further investigate if the very simple mechanism which appears to describe some of the negative ion reactions is generally applicable to such halogen reactions. Further to the work described in this paper, a detailed SIFT survey of the reactions of the rare gas atomic ions with Cl_2 and Br_2 has recently been carried out, the results of which will soon be reported [15].

ACKNOWLEDGEMENTS

APPENDIX I.

The four exothermic atom exchange reactions (7), (8), (9) and (10) seem to be very simple in that they appear to proceed with the formation of the triatomic ion complex, e.g. FCl_2^-, at the collision rate described by the Langevin collisional rate coefficient, k_c, which then separates partly backwards to reactants and partly forward to products (coefficient k_f), for example thus:

$$F^- + Cl_2 \underset{1-k_f}{\overset{k_c}{\rightleftharpoons}} (FCl_2^-)^* \overset{}{\underset{k_f}{\longrightarrow}} Cl^- + ClF$$
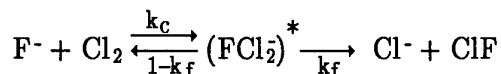
All four reactions are exothermic to the right but not greatly so. It thus appears that the excess energy (the exothermicity of the reaction) of the intermediate

excited ion $(FCl_2^-)^*$ does not significantly influence the course of the reaction, but rather it is the number of available states in the reactants (i.e. F^- and Cl_2) and the products (i.e. Cl^- and ClF) that have the dominant influence. In short, it seems as if the reactions are proceeding in the high temperature limit where enthalpy change is unimportant and when the entropy change controls the branching into two "product" channels. Assuming this to be so, we can calculate the "effective equilibrium constant" for the reaction $K_{eff}=k_f/(1-k_f)$ from the total partition functions, q, of the reactants and products. Thus:

$$K_{eff} = \frac{k_f}{1-k_f} = \frac{q_{Cl^-} \, q_{ClF}}{q_{F^-} \, q_{Cl_2}} = \left[\frac{m_{Cl^-} \, m_{ClF}}{m_{F^-} \, m_{Cl_2}}\right]^{3/2} \cdot \frac{\sigma_{Cl_2}}{\sigma_{ClF}} \cdot \frac{I_{ClF}}{I_{Cl_2}} \cdot \frac{1 - \exp(-h\nu_{Cl_2}/kT)}{1 - \exp(-h\nu_{ClF}/kT)}$$

Here we include the only translational, rotational and vibrational partition functions. (No excited electronic states of the products are accessible, and there is no change in the multiplicity and so electronic partition functions need not be included). Using the data on the bond lengths and the vibrational frequencies for the molecules from Herzberg [18] and the appropriate symmetry numbers, σ, (homomolecular diatomics=2, heteronuclear diatomics=1) we have calculated K_{eff} for the four reactions and obtained the results in parentheses:

$F^- + Cl_2$ (1.53); $F^- + Br_2$(1.67); $I^- + Cl_2$(2.29); $I^- + Br_2$(2.28)
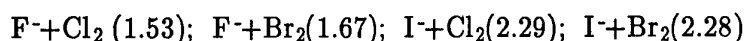
Hence, the $k/k_c = k_f = K_{eff}/(1+K_{eff})$ can be calculated for each reaction and compared with the experimental values. The agreement is quite remarkable as can be seen by scrutinizing the ratios given in Table III as k/k_c and $(k/k_c)^*$.

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CAPTIONS TO TABLES:

Table I: Ionization potentials (I.P.), electron affinities (E.A.) and bond dissociation energies (D, at 298 K) of the atoms and molecules indicated that have been used to calculate the ergicities of the reactions included in this study. All the values are in electronvolts (eV). The I.P. of the halogen atoms into the different spin–orbit states of their positive ions were taken from [10]; the rest of the data was taken from [18].

Table II: The rate coefficients (k) and the product ion distributions for the reactions of F^+, Cl^+, Br^+, I^+, Cl_2^+ and Br_2^+ with Cl_2 and Br_2. The measured k are quoted as, for example 1.1(−9) meaning $1.1 \times 10^{-9} cm^3 s^{-1}$, and in square brackets in the same style are the collisional rate coefficients, k_c, calculated using the Langevin expression [12]. Note that k/k_c is at a maximum (unity) for the $Cl^+ + Br_2$ reaction. The product distributions, given at percentages following the product ions, have been adjusted to account for the spread of the product ion peaks due to the isotopes of chlorine and bromine.

[a]Apparently no reactions occurred, but these reactions presumably proceed via resonant charge transfer which could be checked using isotopically labeled gases.

Table III: The rate coefficients (k) and the product ion distributions for the reactions of F^-, Cl^-, Br^-, I^-, Cl_2^- and Br_2^- with Cl_2 and Br_2. The rate coefficients, k and k_c, and the product distributions are quoted in the same style as in Table II. The $(k/k_c)^*$ are the calculated values obtained from a consideration of partition functions (see text and Appendix I).

[a]Apparently no reactions occurred, but these reactions presumably proceed via resonant electron transfer which could be checked using isotopically labeled gases (see also the comments in the text).

[b]$^{35}Cl^-$ was injected as a primary ion and isotopically mixed Cl_2 was used as the reactant gas.

Table I.

	I.P. (eV)	E.A. (eV)	D (eV)
F	$^3P_2$ 17.42 $^3P_1$ 17.47 $^3P_0$ 17.48	3.401	—
Cl	$^3P_2$ 12.97 $^3P_1$ 13.05 $^3P_0$ 13.09	3.613	—
Br	$^3P_2$ 11.84 $^3P_1$ 12.23 $^3P_0$ 12.32	3.364	—
I	$^3P_2$ 10.45 $^3P_1$ 11.33 $^3P_0$ 11.25	3.059	—
Cl_2	11.48±0.01	2.38	2.56
Br_2	10.54±0.03	2.55	2.00
ClF	...	...	2.66
BrF	...	...	2.59
BrCl	11.1±0.2	...	2.26
ICl	10.07	...	2.19
IBr	9.98±0.03	2.55	1.86

Table II.

	Cl_2			Br_2		
	k	k_c	k/k_c	k	k_c	k/k_c
F^+	$Cl^+(65)$ $Cl_2^\ddagger(35)$			$Br^+(85)$ $Br_2^\ddagger(15)$		
	4.4(–10)	[1.3(–9)]	0.34	8.7(–10)	[1.5(–9)]	0.58
Cl^+	$Cl_2^\ddagger(100)$			$Br_2^\ddagger(100)$		
	5.4(–10)	[1.0(–9)]	0.52	1.2(–9)	[1.2(–9)]	1.01
Br^+	$Cl_2^\ddagger(55)$ $BrCl^+(45)$			$Br_2^\ddagger(100)$		
	6.1(–10)	[8.2(–10)]	0.74	5.2(–10)	[8.6(–10)]	0.61
I^+	$ICl^+(100)$			$IBr^+(80)$ $Br_2^\ddagger(20)$		
$^3P_2$	4.5(–11)	[7.5(–10)]	0.06	6.6(–10)	[7.4(–10)]	0.90
$^3P_{1,0}$	2–4(–10)		0.25–0.5			
$Cl_2^\ddagger$				$Br_2^\ddagger(98)$ $BrCl^+(2)$		
	... a			6.3(–10)	[8.8(–10)]	0.71
$Br_2^\ddagger$	no reaction (k<1(–12))			... a		

x